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AN ASSESSMENT OF THE CHESS SULFATE AND NITRATE DATA During the Period WE/A Performed the Chemical Analysis

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16. ABSTRACT

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In Rockwell's reanalyses, the difference in RETA's sulfate data showed a mean ratio of 51%, but the results on nitrates were inconclusive. The effects of time and handling were not conclusively determined, although there was an indication that nitrates decompose with timelapse more significantly than sulfates. Based on the results of this report, it was recommended that CHESS measurements for sulfates be increased by 51% for all sites for the entire period RETA performed these analyses.

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during the period RETA performed the chemical analysis

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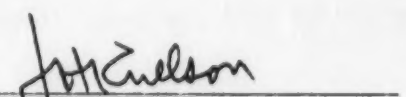
FOREWORD

The many benefits of our modern, developing, industrial society are accompanied by certain hazards. Careful assessment of the relative risk of existing and new man-made environmental hazards is necessary for the establishment of sound regulatory policy. These regulations serve to enhance the quality of our environment in order to promote the public health and welfare and the productive capacity of our Nation's population.

The Health Effects Research Laboratory, Research Triangle Park conducts a coordinated environmental health research program in toxicology, epidemiology, and clinical studies using human volunteer subjects. These studies address problems in air pollution, non-ionizing radiation, environmental carcinogenesis and the toxicology of pesticides as well as other chemical pollutants. The Laboratory develops and revises air quality criteria documents on pollutants for which national ambient air quality standards exist or are proposed, provides the data for registration of new pesticides or proposed suspension of those already in use, conducts research on hazardous and toxic materials, and is preparing the health basis for non-ionizing radiation standards. Direct support to the regulatory function of the Agency is provided in the form of expert testimony and preparation of affidavits as well as expert advice to the Administrator to assure the adequacy of health care and surveillance of persons having suffered imminent and substantial endangerment of their health.

This study addresses a concern regarding some of the air pollution measurements collected in the CHESS air monitoring system. Severe manpower limitations forced the Health Effects Research Laboratory to contract for the chemical analysis of high-volume filter strips. Some measurement effects resulted, and this paper investigates the nature of the differences and recommends an appropriate procedure.



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Director,
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ABSTRACT

In the early 1970s certain filters from the CHESS network were collected and sent to the Human Studies Laboratory Bioenvironmental Laboratory Branch (BELB) for sulfate and nitrate analyses. These analyses were interrupted on October 1, 1972 and subsequently continued under contract signed March 1973 with Rickman, Edgerley, Tomlinson, and Associates (RETA). Many of the filters were not analyzed until RETA became fully operational in May 1973, whereupon their measurements began to be inexplicably and consistently low.

The disparity between HSL results and RETA's findings engendered an investigation involving reanalyses to verify the apparent disparity, and then to determine a statistical adjustment factor to correct for anomalies. In November 1974 Rockwell International undertook the reanalyses of these CHESS filters.

In Rockwell's reanalyses, the difference in RETA's sulfate data showed a mean ratio of 51%, but the results on nitrates were inconclusive. The effects of time and handling were not conclusively determined, although there was an indication that nitrates decompose with timelapse more significantly than sulfates. Based on the results in this report, it was recommended that CHESS measurements for sulfates be increased by 51% for all sites for the entire period RETA performed these analyses.

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SECTION 1

INTRODUCTION

The sulfate and nitrate fractions of total suspended particulate Community Health Environmental Surveilance Systems (CHESS) data showed a dramatic and sustained decrease beginning in September and October of 1972. A review of the data in Tables 1 through 4 indicates that the sudden decrease was not an isolated incident, but that a peculiarity existed across CHESS sites and the drop could not be attributed solely to seasonal variation.

Tables 1 and 2 show the sulfate ratios of the quarterly arithmetic means to the respective 1973 quarterly arithmetic means by site. The sulfate ratios for the first three quarters are generally similar through 1972, but drop in 1973. However, the fourth quarter ratios show the decrease in 1972, and it is sustained in 1973.

The nitrate ratios displayed in Tables 3 and 4 show similar decreases, although they also show a difference between 1970 and 1971 that has never been explained.

It is unlikely that this across-the-board decrease could have been caused by a decrease in actual pollutant levels. An investigation by Environmental Monitoring and Support Laboratory (EMSL) could uncover no significant Federal or State sulfur regulations that were implemented for the first time during the period in question.

The most obvious source of error was a change in the laboratories responsible for the sulfate and nitrate analyses. On October 1, 1972 the

Bioenvironmental Laboratory Branch (BELB) of the Human Studies Laboratory (HSL), now Health Effects Research Laboratory (HERL), ceased analysis of sulfates and nitrates, and exposed filters received after that date were stored for future analysis. A contract was signed in March 1973, turning over the sulfate and nitrate analyses to Ryckman, Edgerley, Tomlinson, and Associates (RETA). The same analytical methods used by HSL, BELB, were also used by RETA. RETA was not fully operational until May 1973 and had the difficult responsibility of overcoming the backlog of filters -- which were not stored and shipped under the most desirable conditions. Therefore, many of the filters were not actually analyzed until May and June of 1973.

The effects of this excessive handling and delays in analyzing the filters cannot be determined. However, it was felt that the decrease in pollutant levels was so large, and was sustained for so long, that the problem entailed more than excessive handling and delays in analyzing the filters. Therefore, the purpose of this report is to show whether or not RETA's laboratory procedures produced erroneous results, and if so, how the existing data base can be adjusted to account for the errors.

Quality control efforts were minimal during the period in which RETA was performing the analysis. However, our investigation did turn up several sets of data which were related to the problem.

The Human Studies Laboratory conducted an experiment in November 1974 in which Rockwell International (the current contracted laboratory) reanalyzed some 219 filters which had been analyzed initially by RETA and HSL. This experiment provides the most direct approach to the problem, and our conclusions and recommendations are based primarily on it.

SECTION 2

OTHER STUDIES RELATED TO THE PROBLEM

Scattered attempts were made by various groups to check the quality of RETA's output during the period in question. However, a unified approach to the problem was sorely lacking.

In these experiments (see Appendix), the problem was approached in four ways: 1) a second laboratory "reanalyzed" exposed filters which had been analyzed some time earlier, 2) two laboratories analyzed the "same" exposed filters simultaneously, 3) one or more laboratories analyzed the "same" solutions of known concentrations, and 4) two laboratories analyzed the "same" spiked filters of known concentrations.

RETA showed good reproducibility of HSL analyses in April 1973, just before RETA became operational. However, in June 1974, RETA's reanalysis of filters was different from earlier analyses by both RETA and HSL.

When RETA and QAEML analyzed the "same" filters simultaneously in April through June 1974, RETA's measurements were significantly lower.

In July 1974, RETA consistently understated concentrations of spiked filters.

SECTION 3

ROCKWELL'S REANALYSIS OF CHESS FILTERS

GENERAL PROCEDURES

In November 1974, 219 filters from the CHESS network were retrieved, and new strips were cut from them and shipped to Rockwell for reanalysis for sulfates and nitrates. The original design called for one filter per month per 12 stations from July 1972 through June 1974, but almost one-third of the filters could not be reanalyzed, either because they were in poor condition or they could not be located.

Twenty-two of these filters had been initially analyzed by HSL and the other 197 by RETA. They were selected at random from high-exposure and low-exposure sites in Charlotte, Birmingham, Chattanooga, New York, Utah, and California.

In addition to these 219 filters, 62 other filters were sent to Rockwell for reanalysis. These filters were originally analyzed by RETA, then set aside for quality control purposes in June 1973 and never utilized. Since these filters were stored in glassine envelopes, it was felt that they were better preserved than the others.

Statistical Analysis

An analysis of variance was performed on the 219 filter results to test for possible effects of sites, days between exposure and reanalysis, and the laboratory which did the first analysis. The first concentration was considered one of the independent variables and the second concentration was analyzed as the dependent variable.

The concentrations, unless otherwise stated, are in micrograms per cubic meter ($\mu g/m^3$).

The results in Table 5 show no effects of time or sites, but show strong influences from the first concentration and from the laboratory which did the first analysis.

To make a valid comparison between the laboratories we must have them both operating on the same experimental material. Thus, we must make three assumptions:

- First, since a second strip was cut from the filter for the reanalysis, we must assume the pollutant concentration is uniform across the filter. However, we are not aware of any documentation on this point.
- Second, we assume no change in pollutant amount between analyses due to the handling of the filters.
- Third, the natural pollutant decomposition over time was assumed to be negligible. It was generally felt that this is a valid assumption for sulfates, but some scientists feel that nitrates decompose by a significant amount.

Subject to the above three assumptions, the data set can be thought of as n pairs of realizations of the log-normally distributed random variables, x and y. Since the filters were pulled from a population at random, we can assume that the random variables $X = \ln x$ and $Y = \ln y$ have a bivariate normal distribution with means μ_x^2 and μ_y^2, variances σ_x^2 and σ_y^2 and correlation coefficent ρ.

Then the random variable $Z = X - Y$ is normally distributed with mean $\mu_z = \mu_x - \mu_y$ and variance $\sigma_z^2 = \sigma_x^2 + \sigma_y^2 - 2\rho\sigma_x\sigma_y$. The fact that $\exp(Z) = x/y$ enables us to make inferences about the ratio of the random variables x and y.

It was felt that gross violations of the first two assumptions would be

manifest as outliers. Therefore, the criterion for labeling an observation as an outlier and excluding it from the analysis was based on the ratio.

If we represent the sample arithmetic mean by $\bar{Z}$ and the sample variance by S^2, we know that the statistic $t=(\bar{Z}-\mu_z)/(S/\sqrt{n-1})$ is distributed as Student's t with n-1 degrees of freedom. Then t is used to test the hypothesis that $\mu_z=0$, or equivalently that x=y. Confidence intervals are constructed for μ_z, which is the geometric mean of the ratio x/y.

The computer printouts show the descriptive statistics for x and y (the numerator in the ratio is listed first, then the denominator in the second column) along with the value of t and the 95% confidence interval for μ_z. The value of t is significant at the 0.05 level if and only if the confidence interval includes one.

Table 6 shows the results of Rockwell's reanalysis of the 197 filters originally analyzed by RETA. RETA is 43-60% low on sulfates, with a mean ratio of 51%, but there is no significant difference on nitrates.

The data from the 62 filters which were stored in glassine envelopes are analyzed in Table 7. RETA comes up 22-35% low on sulfates, but 31-55% high on nitrates.

The 22 filters which were first analyzed by HSL are analyzed in Table 8. There is no significant difference on sulfates, but HSL is 18-66% high on nitrates.

The filters initially analyzed by RETA were divided into three groups to see if this breakdown would show an effect that the analysis of variance did not show. The first group, filters exposed between September 1972, and June 1973, were the backlogged filters which were more physically abused. The second group, filters exposed between July 1973, and December 1973, were

analyzed on a more timely basis. The other group of filters exposed in 1974 were analyzed on RETA's regular schedule -- within three weeks of exposure.

A comparison of the results in Tables 9 - 11 with Table 6 shows no group effect. The sulfate intervals are 36-60%, 32-70%, and 48-72% respectively, all of which contain 51%. None of the three groups show a significant difference for nitrates.

The ratio of Rockwell to RETA is plotted against the RETA measurement for each time group in Figures 1-3. The plots indicate that the ratio does not depend on pollutant level.

SECTION 4

CONCLUSIONS

We recommend that sulfates be increased by 51% for all CHESS sites for the entire time period RETA performed the analyses.

We believe there is a decomposition effect with nitrates, as evidenced by the Tables 7 and 8. Since we could not detect a difference between RETA and Rockwell on the 197 filters, we cannot recommend a nitrate adjustment. However, if decomposition prevented a valid comparison, an independent study to quantify that effect could enable us to formulate a nitrate adjustment factor.

TABLE 1. RATIO OF SULFATE QUARTERLY ARITHMETIC MEAN TO 1973 QUARTERLY ARITHMETIC MEAN - - FIRST AND SECOND QUARTERS

Site	1st Quarter				2nd Quarter			
	70	71	72	73	70	71	72	73
0211	2.36	1.62	1.76	1.00	1.90	1.51	1.41	1.00
0221	1.61	1.24	1.34	1.00	1.83	1.58	1.41	1.00
0232	2.74	1.95	2.10	1.00	2.09	1.54	1.65	1.00
0312		1.33	1.80	1.00		1.63	1.89	1.00
0323		2.26	2.89	1.00		1.31	1.33	1.00
0331	1.78	1.50	1.86	1.00	2.27	1.75	1.67	1.00
0411		2.54	2.80	1.00		1.10	1.51	1.00
0421		2.25	2.31	1.00		1.26	1.41	1.00
0431		2.03	1.92	1.00		1.38	1.49	1.00
0811		0.92	1.16	1.00		1.87	2.23	1.00
0821		0.82	0.87	1.00		1.79	2.54	1.00
0831		0.81	0.78	1.00		1.50	1.69	1.00
0841		0.80	0.84	1.00		1.11	1.48	1.00
0621		1.18	1.00	1.00		1.10	1.56	1.00
0622		1.03	1.10	1.00		1.38	1.42	1.00
0631		1.03	1.05	1.00		0.81	0.89	1.00
0632		1.50	1.56	1.00		1.61	1.51	1.00
0633		1.55	2.14	1.00		1.41	1.47	1.00
0634		1.11	1.48	1.00		1.37	1.48	1.00
0635		1.74	1.98	1.00		1.43	1.35	1.00
0641		1.27	1.54	1.00		1.32	1.34	1.00
0642		1.29	1.88	1.00		1.28	1.56	1.00

(CONTINUED)

TABLE 1 (continued)

Site	1st Quarter				2nd Quarter			
	70	71	72	73	70	71	72	73
0711			2.27	1.00		0.87	1.72	1.00
0721			1.82	1.00		0.76	1.58	1.00
0722			1.79	1.00		0.72	1.48	1.00
0732			1.90	1.00			1.71	1.00
0811			3.97	1.00			1.79	1.00
0821				1.00			1.15	1.00
0822				1.00			1.18	1.00
0831			5.61	1.00			1.26	1.00
0832				1.00			1.17	1.00
0841			5.80	1.00			1.23	1.00
0842				1.00			1.23	1.00

TABLE 2. RATIO OF SULFATE QUARTERLY ARITHMETIC MEAN TO 1973 QUARTERLY ARITHMETIC MEAN - - THIRD AND FOURTH QUARTERS

Site	3rd Quarter				4th Quarter			
	70	71	72	73	70	71	72	73
0211	1.16	0.95	1.14	1.00	1.82	1.98	1.20	1.00
0221	1.09	1.03	1.09	1.00	1.49	1.90	0.67	1.00
0232	1.47	1.22	1.24	1.00	1.96	2.08	1.06	1.00
0312		1.41	1.61	1.00	1.64	1.57	1.05	1.00
0323		1.16	1.45	1.00	1.79	1.63	1.14	1.00
0331	1.52	1.30	1.40	1.00	2.22	2.07	1.44	1.00
0411		1.28	1.35	1.00	3.13	2.91	0.94	1.00
0421		1.23	1.16	1.00	2.27	2.11	0.86	1.00
0431		1.28	1.18	1.00	2.33	2.44	1.00	1.00
0511		1.52	1.12	1.00		3.45	1.72	1.00
0521		1.43	1.37	1.00		2.86	1.71	1.00
0531		1.35	1.18	1.00		2.44	1.68	1.00
0541		1.18	1.01	1.00		1.48	1.07	1.00
0611	1.41	1.10	1.35	1.00	1.67	1.73	1.16	1.00
0612	1.00	1.01	1.03	1.00	1.67	1.60	0.97	1.00
0631	1.46	1.19	1.38	1.00	1.72	1.60	1.21	1.00
0632	1.62	1.29	1.26	1.00	1.47	1.53	1.01	1.00
0633	1.64	1.43	1.60	1.00	1.88	1.81	1.23	1.00
0634	1.80	1.27	1.64	1.00	1.75	1.82	1.39	1.00
0635	1.46	1.19	1.38	1.00	1.92	1.92	1.16	1.00
0641	1.52	1.10	1.47	1.00	1.82	1.89	1.13	1.00
0642	1.23	1.00	1.30	1.00	1.75	1.75	1.18	1.00

(CONTINUED)

TABLE 2 (continued)

Site	3rd Quarter				4th Quarter			
	70	71	72	73	70	71	72	73
0711*		1.18	1.00			2.56	1.00	
0721*		1.08	1.00			2.50	1.00	
0722*		1.11	1.00			2.04	1.00	
0732*			1.00				1.00	
0811			0.84	1.00			0.72	1.00
0821			0.79	1.00			0.73	1.00
0822			0.82	1.00			0.63	1.00
0831			0.75	1.00			0.57	1.00
0832			0.81	1.00			0.57	1.00
0841			0.85	1.00			0.55	1.00
0842			0.77	1.00			0.71	1.00

* NEW JERSEY DENOMINATORS ARE 1972 QUARTERLY MEANS

TABLE 3. RATIO OF NITRATE QUARTERLY ARITHMETIC MEAN TO 1973 QUARTERLY ARITHMETIC MEAN - - FIRST AND SECOND QUARTERS

Site	1st Quarter				2nd Quarter			
	70	71	72	73	70	71	72	73
0211	1.50	1.00	2.17	1.00	1.50	3.00	1.50	1.00
0221	1.00	0.69	1.23	1.00	1.50	3.17	1.67	1.00
0232	2.00	1.22	2.00	1.00	1.57	3.00	1.57	1.00
0312		1.23	1.30	1.00		2.89	1.56	1.00
0323		1.36	1.29	1.00		2.21	1.21	1.00
0331	1.56	1.22	1.28	1.00	1.64	2.50	1.43	1.00
0411		1.18	2.36	1.00		1.25	1.75	1.00
0421		1.21	2.86	1.00		1.86	2.14	1.00
0431		1.00	1.95	1.00		2.33	1.83	1.00
0511		0.50	1.00	1.00		3.20	2.80	1.00
0521		0.71	1.58	1.00		3.14	2.14	1.00
0531		0.80	2.40	1.00		2.29	1.57	1.00
0541		1.21	4.86	1.00		3.00	2.00	1.00
0621		2.40	3.00	1.00		5.14	2.14	1.00
0622		1.62	2.46	1.00		4.57	1.86	1.00
0631		19.75	11.00	1.00		3.83	1.38	1.00
0632		3.60	3.40	1.00		5.33	2.78	1.00
0633		6.12	5.62	1.00		7.00	3.13	1.00
0634		5.50	5.67	1.00		7.14	3.29	1.00
0635		2.40	2.70	1.00		6.00	3.00	1.00
0641		3.14	2.71	1.00		4.00	1.57	1.00
0642		1.60	1.90	1.00		3.43	1.71	1.00

(continued)

TABLE 3 (continued)

S'te	1st Quarter				2nd Quarter			
	70	71	72	73	70	71	72	73
0711			2.23	1.00		9.00	3.00	1.00
0721			1.94	1.00		5.63	2.63	1.00
0722			2.00	1.00		3.20	1.50	1.00
0732			2.00	1.00			2.25	1.00
0811			4.36	1.00			2.17	1.00
0821				1.00			1.41	1.00
0822				1.00			2.08	1.00
0831			3.89	1.00			1.95	1.00
0832				1.00			1.71	1.00
0841			7.79	1.00			3.27	1.00
0842				1.00			2.60	1.00

TABLE 4. RATIO OF NITRATE QUARTERLY ARITHMETIC MEAN TO 1973 QUARTERLY ARITHMETIC MEAN -- THIRD AND FOURTH QUARTERS

Site	3rd Quarter				4th Quarter			
	70	71	72	73	70	71	72	73
0211	1.00	4.50	2.00	1.00	0.71	2.86	0.86	1.00
0221	2.50	8.50	2.00	1.00	0.70	2.50	0.80	1.00
0232	2.00	9.50	2.50	1.00	0.80	2.80	0.80	1.00
0312		3.85	2.23	1.00	0.85	2.08	1.00	1.00
0323	1.45	2.23	1.57	1.00	0.67	1.67	0.80	1.00
0331	1.49	2.07	1.24	1.00	0.65	1.65	1.00	1.00
0411		3.45	1.48	1.00	1.27	2.80	0.81	1.00
0421		4.55	1.88	1.00	1.00	2.89	0.61	1.00
0431	1.00	4.00	2.00	1.00	0.94	3.01	0.59	1.00
0511		3.23	1.61	1.00	3.70	2.81	1.00	1.00
0521		3.23	1.32	1.00	1.67	3.00	1.17	1.00
0531		2.33	1.33	1.00	1.16	3.57	0.83	1.00
0541		3.45	1.83	1.00	1.16	2.57	0.50	1.00
0621	3.57	4.96	2.00	1.00	1.89	3.87	1.09	1.00
0622	2.63	7.89	2.32	1.00	2.22	4.67	1.00	1.00
0631	4.00	6.08	7.40	1.00	4.00	3.76	1.48	1.00
0632	2.78	6.94	3.97	1.00	1.69	3.54	1.00	1.00
0633	2.38	5.76	3.57	1.00	2.33	4.42	0.77	1.00
0634	5.56	18.67	9.60	1.00	3.85	9.39	0.85	1.00
0635	2.00	7.26	3.76	1.00	2.27	3.20	0.68	1.00
0641	1.49	4.73	1.49	1.00	1.41	2.32	0.66	1.00
0642	1.00	4.00	1.50	1.00	1.56	2.67	0.67	1.00

(continued)

TABLE 4 (continued)

Site	3rd Quarter				4th Quarter			
	70	71	72	73	70	71	72	73
0711*		2.08	1.00			5.00	1.00	
0721*		3.45	1.00			5.26	1.00	
0722*		2.72	1.00			4.17	1.00	
0732*			1.00			3.03	1.00	
0811			2.70	1.00			1.03	1.00
0821			1.85	1.00			0.91	1.00
0822			3.85	1.00			0.67	1.00
0831			3.13	1.00			0.42	.00
0832			2.56	1.00			0.85	1.00
0841			3.23	1.00			0.81	1.00
0842			3.23	1.00			0.62	1.00

*NEW JERSEY DENOMINATORS ARE 1972 QUARTERLY MEANS

TABLE 5. ANALYSIS OF VARIANCE FOR ROCKWELL'S REANALYSIS

Sulfates

Factor	d.f.	Partial S.S.	F value	p
Initial Concentration	1	26280.2	644.85	0.000
Days Between Exposure and Reanalysis	1	83.3	2.04	0.154
Sites	1	124.0	3.04	0.083
Laboratories	1	401.4	9.85	0.002

Nitrates

Factor	d.f.	Partial S.S.	F value	p
Initial Concentration	1	868.9	248.40	0.000
Days Between Exposure and Reanalysis	1	11.6	3.32	0.070
Sites	1	5.8	1.66	0.199
Laboratories	1	33.2	9.49	0.002

TABLE 6. NOVEMBER 1974 - ROCKWELL REANALYZED 200 RETA FILTERS

Statisitics	Sulfates		Nitrates	
Geometric Mean Ratio	1.512		0.936	
95% Confidence Interval for Geometric Mean Ratio	(1.433, 1.597)		(0.854, 1.025)	
Correlation Coefficient of Logs	0.8672		0.8166	
Number of Observations	190		186	
	Rockwell	RETA	Rockwell	RETA
Arithmetic Mean	17.644	12.519	3.031	3.228
Geometric Mean	14.979	9.904	1.853	1.980
Maximum	111.700	76.800	16.200	21.100
Minimum	3.700	0.900	0.090	0.090
Standard Deviation	12.582	9.021	3.108	3.519
Geometric Standard Deviation	1.741	2.102	2.877	2.814

TABLE 7. NOVEMBER 1974 - ROCKWELL REANALYZED "GLASSINE" FILTERS

Statistics	Sulfates		Nitrates	
Geometric Mean Ratio	1.282		0.556	
95% Confidence Interval for Geometric Mean Ratio	(1.220, 1.347)		(0.451, 0.686)	
Correlation Coefficient of Logs	0.9514		0.7612	
Number of Observations	60		62	
	Rockwell	RETA	Rockwell	RETA
Arithmetic Mean	22.703	18.502	1.049	1.290
Geometric Mean	20.237	15.789	0.514	0.925
Maximum	58.600	75.300	5.400	4.400
Minimum	5.500	2.700	0.090	0.090
Standard Deviation	10.500	10.764	1.212	0.965
Geometric Standard Deviation	1.659	1.822	3.652	2.525

TABLE 8. NOVEMBER 1974 - ROCKWELL REANALYZED HSL'S FILTERS

Statistics	Sulfates		Nitrates	
Geometric Mean Ratio	1.034		0.530	
95% Confidence Interval for Geometric Mean Ratio	(0.944, 1.133)		(0.341, 0.822)	
Correlation Coefficient of Logs	0.9331		0.7694	
Number of Observations	20		22	
	Rockwell	HSL	Rockwell	HSL
Arithmetic Mean	25.465	24.765	2.135	3.609
Geometric Mean	22.508	21.761	0.785	1.482
Maximum	52.400	51.700	9.200	19.000
Minimum	9.500	7.200	0.090	0.090
Standard Deviation	12.288	12.550	2.976	5.192
Geometric Standard Deviation	1.696	1.714	4.427	4.156

TABLE 9. NOVEMBER 1974 - ROCKWELL REANALYZED NINE BAD MONTHS

Statistics	Sulfates		Nitrates	
Geometric Mean Ratio	1.471		1.075	
95% Confidence Interval for Geometric Mean Ratio	(1.352, 1.601)		(0.967, 1.196)	
Correlation Coefficient of Logs	0.8555		0.8719	
Number of Observations	90		85	
	Rockwell	RETA	Rockwell	RETA
Arithmetic Mean	16.740	12.270	3.320	3.199
Geometric Mean	14.045	9.547	2.165	2.013
Maximum	111.700	76.800	13.400	17.500
Minimum	3.700	0.900	0.200	0.090
Standard Deviation	12.852	9.555	3.052	3.404
Geometric Standard Deviation	1.774	2.166	2.656	2.713

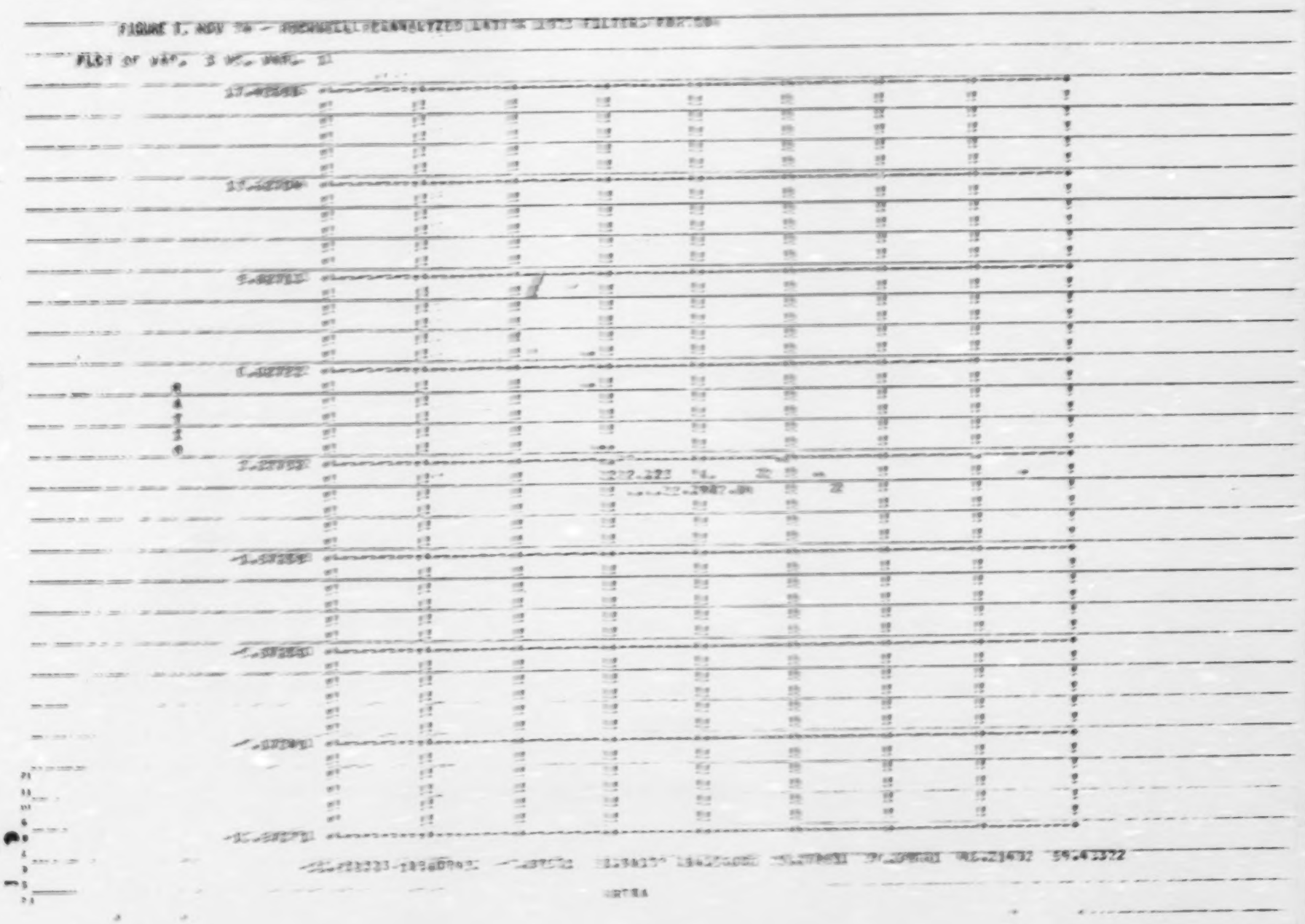
TABLE 10. NOVEMBER 1974 - ROCKWELL REANALYZED LATTER 1973 FILTERS

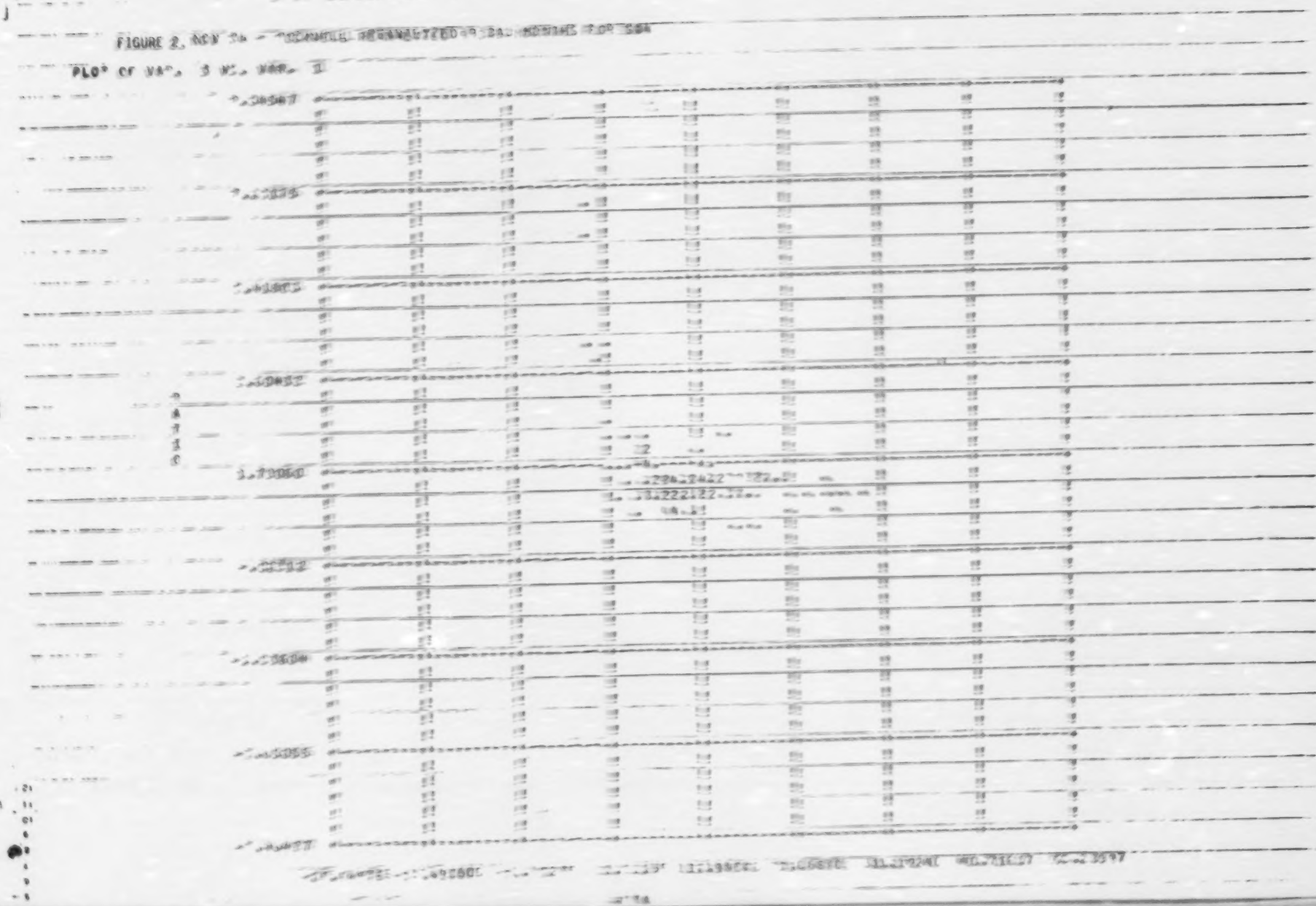
Statistics	Sulfates		Nitrates	
Geometric Mean Ratio	1.496		0.793	
95% Confidence Interval for Geometric Mean Ratio	(1.318, 1.698)		(0.619, 1.016)	
Correlation Coefficient of Logs	0.9037		0.7597	
Number of Observations	44		45	
	Rockwell	RETA	Rockwell	RETA
Arithmetic Mean	20.239	14.836	2.651	3.264
Geometric Mean	16.052	10.732	1.438	1.813
Maximum	92.100	54.300	16.200	14.000
Minimum	4.700	0.900	0.090	0.090
Standard Deviation	17.042	11.322	3.176	3.424
Geometric Standard Deviation	1.923	2.497	3.348	3.457

TABLE III. NOVEMBER 1974 – ROCKWELL REANALYZED EARLY 1974 FILTERS

Statistics	Sulfates	Nitrates
Geometric Mean Ratio	1.595	0.986
95% Confidence Interval for Geometric Mean Ratio	(1.482, 1.777)	(0.764, 1.007)
Correlation Coefficient of Logs	0.8407	0.8277
Number of Observations	56	56

	Rockwell	REEA	Rockwell	KETA
Arithmetic Mean	17.857	11.1000	2.896	3.245
Geometric Mean	15.734	9.9865	1.793	2.072
Maximum	28.300	220.7000	15.600	21.100
Minimum	6.700	2.7000	0.090	0.300
Standard Deviation	6.525	5.0095	3.151	3.818
Geometric Standard Deviation	1.522	1.6677	2.771	2.499





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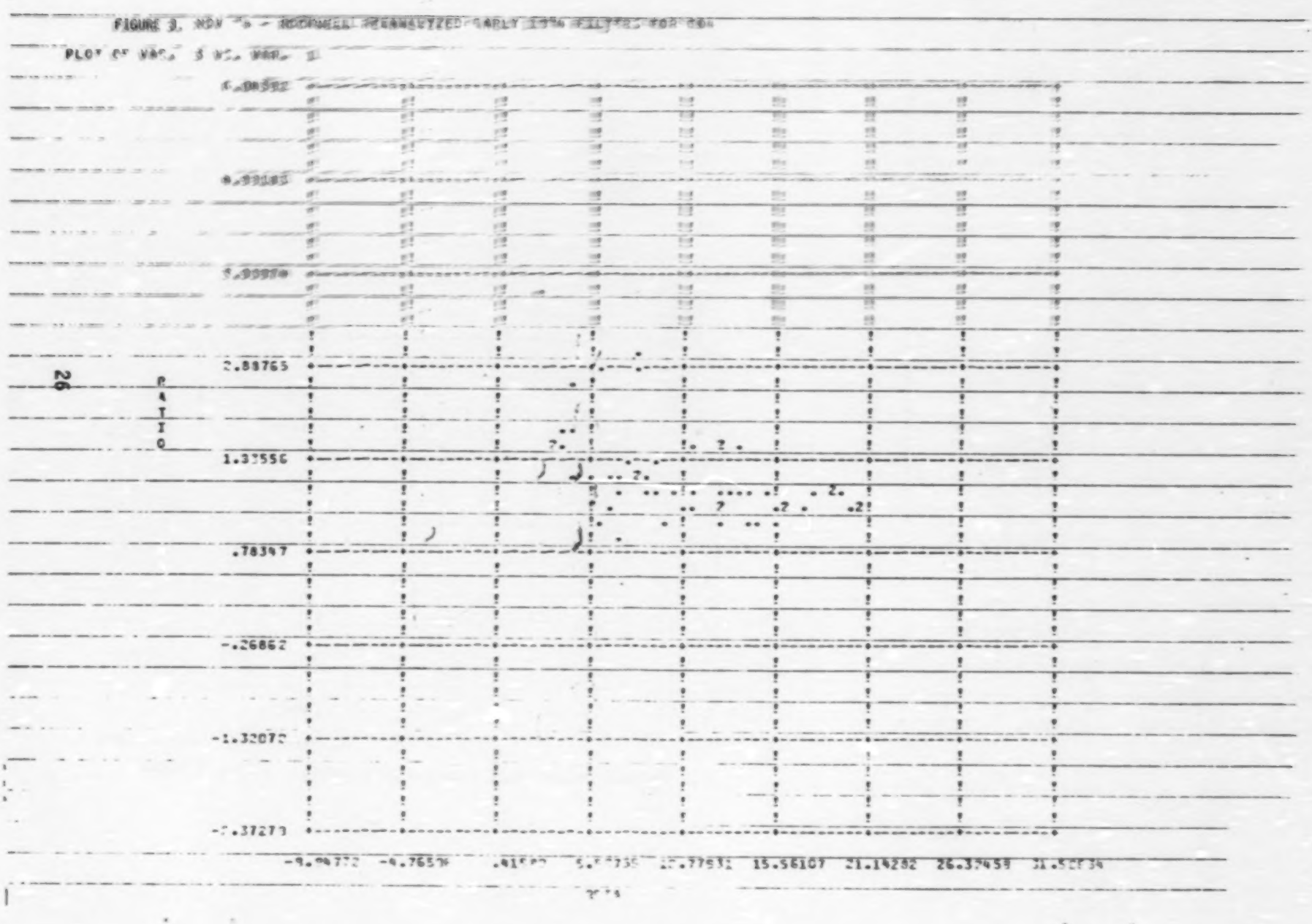

FIGURE 3. NOV '6 - ROCKWELL DEEMPHASIZED EARLY 1976 FILTER, FOR 204

APPENDIX

EXPERIMENTS INVOLVING THE REANALYSIS OF EXPOSED FILTERS

The same rationale that was used in the Statistical Analysis of the Rockwell experiment in the text is used here.

1.A. (Table A-1) In April 1973, several weeks before RETA was fully operational, 10 filters from the CHESS network which had been analyzed by HSL in September 1972 were flown to St. Louis to have RETA reanalyze them for sulfates.

The data are in milligrams per filter, so the values would have to be approximately halved to convert to micrograms per cubic meter. Table A-11 contains conversion factors for the different units used in these studies.

The analysis shows a laboratory difference, but it is only 3-15%. In the absence of any standards to go by, this was, and still is, considered good agreement.

1.B. (Tables A-2 and A-3) In June 1974, RETA was asked to reanalyze 30 filters exposed in the CHESS network in September and October 1972. Eighteen of the filters were initially analyzed by RETA, and the remaining 12 were analyzed first by HSL.

Table A-2 shows the results for the 18 filters first analyzed by RETA. The 1974 analyses were 1-15% higher than 1972 for sulfates, but were 13-32% higher than 1972 for nitrates.

Table A-3 compares RETA 1974 vs. HSL 1972. RETA's sulfate measurements were 35-108% lower than HSL's. The RETA nitrate values were also well below HSL's, but the correlation between nitrate values was a low 0.478.

EXPERIMENTS COMPARING LABORATORIES ANALYZING THE SAME FILTERS SIMULTANEOUSLY

In the experiments, two strips were cut from the filter and one given to each laboratory for analysis. Thus, we need to make the assumption of uniformity of pollutant concentration across the filter. However, the other two assumptions are not necessary, as there is no timelag between analyses.

Statistical Analysis

The same approach was used on these data sets that was used on the experiments involving reanalysis of exposed filters.

2.A. (Table A-4) In April and May 1974, 13 filters were given to RETA and QAEML for a laboratory comparison for both sulfates and nitrates.

The measurements showed high correlations, but RETA was 23-41% low on sulfates and 26-46% low on nitrates.

2.B. (Table A-5) In June 1974, another laboratory comparison involving RETA and QAEML was performed using 16 filters. Only nitrates were analyzed, as this was part of the New York City DAR-CHESS NO_3 Discrepancy Study.

The data are in micrograms per filter strip, so the values would have to be divided by approximately 200 to convert to micrograms per cubic meter.

RETA was 19-30% low on these nitrate measurements.

2.C. (Table A-6) In July 1974, two CHESS hi-vol instruments were located in Garden Grove, California, for 21 days and in Thousand Oaks, Calfornia, for two days. The filters from one instrument were analyzed by RETA and the other by Rockwell.

These data necessitate the further assumption that the pollutant concentration is uniform across the CHESS sites. The Garden Grove instruments were located one mile apart.

There was no significant difference between the RETA and Rockwell measurements of sulfates. RETA was low on nitrates, but the correlation coefficient on nitrates was a very low 0.247.

EXPERIMENTS COMPARING LABORATORIES ANALYZING SPIKED SOLUTIONS

Spiked solutions containing known (unknown to the laboratory) pollutant concentrations were given to each laboratory for analysis. Several levels of concentration were used.

The only assumption needed is that the solutions are homogeneous. If the solution was separated into bottles, aliquots, or otherwise broken down into smaller containers, it needs to be assumed that the concentration would remain the same throughout.

All the data are in micrograms per milliliter, so the values would have to be divided by approximately 3.4 to convert to micrograms per cubic meter.

Statistical Analysis

We assumed that all solutions were identical except for pollutant content, and that level was known without error. The mean response of each laboratory at each level was tabulated, and a 95% confidence interval for that mean was calculated when possible. If the laboratory was functioning correctly, we would expect the confidence interval to include the known level of input.

3.A. (Table A-7) In May 1973, RETA and QAEML were each given five sulfate solutions at each of three levels to check RETA's quality. Both laboratories exhibited errors in measurement, but due to ignorance concerning the method itself, no alarm was sounded.

3.B. (Table A-8) In December 1973, RETA analyzed 16 solutions at two pollutant levels for sulfates and nitrates. Two solutions at each level were analyzed on both the morning and afternoon of each of four days.

An analysis of variance was performed to test for possible time of day and data effects. Neither was significant for sulfates, but both were significant at the 0.05 level for nitrates. The ANOVA table appears with RETA's estimates of the levels in Table A-8.

RETA's accuracy is poor, but these are very low levels, especially for nitrates.

3.C. (Table A-9) In June 1974, as part of the New York City DAR-CHESS NO_3 Discrepancy Study, RETA and QAEML analyzed solutions at six levels of NO_3. QAEML provided one measurement at each level, while RETA analyzed three solutions at each level.

Confidence intervals were not calculated, as RETA's values contained almost no variability. Although RETA appears to obtain lower measurements at higher concentrations, we did not evaluate these differences because of the small sample size and lack of knowledge concerning interlaboratory variablity.

EXPERIMENT INVOLVING ANALYSIS OF SPIKED FILTERS

In July 1974, Rockwell and RETA analyzed five filter strips of known concentration at each of five levels for sulfates and at each of four levels for nitrates.

It has to be assumed that the pollutant concentration was distributed uniformly across the filters.

The data are in milligrams per filter, so the numbers would have to be approximately halved to convert to micrograms per cubic meter.

Statistical Analysis

Mean responses and confidence intervals for the mean responses were tabulated as in Section 3 above.

Table A-10 contains the data showing that RETA is consistently low on both sulfates and nitrates. Rockwell is also low at some levels, but not to the same extent as RETA. A knowledge of interlaboratory variability would enable further inferences to be made from this data set.

CONVERSION FACTORS FOR TABLES

Assuming: Time = 1440 minutes, Flow = 50 cubic feet per minute

Micrograms per Cubic Meter = 2.95×10^{-1} Micrograms per Milliliter

= 5.89×10^{-3} Micrograms per Strip

= 4.91×10^{-4} Micrograms per Filter

TABLE A-1. APRIL 1973 - RETA REANALYZED HSL'S SEPTEMBER 1972 FILTERS

Sulfates

Geometric Mean Ratio	0.906	
95% Confidence Interval for Geometric Mean Ratio	(0.846, 0.970)	
Correlation Coefficient of Logs	0.9818	
Number of Observations	10	
	HSL	RETA
Arithmetic Mean	33.680	36.360
Geometric Mean	31.424	34.676
Maximum	58.200	57.600
Minimum	20.000	23.400
Standard Deviation	13.747	12.307
Geometric Standard Deviation	1.472	1.375

TABLE A-2. JUNE 1974 - RETA REANALYZED RETA'S OCTOBER 1972 FILTERS

Statistics	Sulfates		Nitrates	
Geometric Mean Ratio	1.076		1.222	
95% Confidence Interval for Geometric Mean Ratio	(1.005, 1.153)		(1.134, 1.316)	
Correlation Coefficient of Logs	0.9294		0.9665	
Number of Observations	18		18	
	RETA	Early RETA	RETA	Early RETA
Arithmetic Mean	11.744	11.033	2.527	2.139
Geometric Mean	11.152	10.360	2.341	1.916
Maximum	19.700	19.800	4.950	4.200
Minimum	5.400	4.800	1.140	0.700
Standard Deviation	3.747	3.927	1.004	0.974
Geometric Standard Deviation	1.405	1.453	1.505	1.653

TABLE A-3. JUNE 1974 - RETA REANALYZED HSL'S SEPTEMBER 1972 FILTERS

Statistics	Sulfates		Nitrates	
Geometric Mean Ratio	1.676		2.290	
95% Confidence Interval for Geometric Mean Ratio	(1.350, 2.081)		(1.059, 4.953)	
Correlation Coefficient of Logs	0.9541		0.4776	
Number of Observations	11		12	
	HSL	RETA	HSL	RETA
Arithmetic Mean	13.818	9.327	2.050	1.295
Geometric Mean	11.944	7.125	1.618	0.706
Maximum	24.300	18.600	4.400	3.800
Minimum	4.900	2.100	0.400	0.031
Standard Deviation	7.315	6.226	1.355	1.201
Geometric Standard Deviation	1.798	2.292	2.139	3.962

TABLE A-4. APRIL-MAY 1974 - LABORATORY COMPARISON

Statistics	Sulfates		Nitrates	
Geometric Mean Ratio	1.317		1.357	
95% Confidence Interval for Geometric Mean Ratio	(1.231, 1.410)		(1.257, 1.464)	
Correlation Coefficient of Logs	0.9728		0.9548	
Number of Observations	12		13	
	EMSL	RETA	EMSL	RETA
Arithmetic Mean	8.908	6.708	6.515	4.800
Geometric Mean	8.125	6.158	6.069	4.473
Maximum	15.800	10.900	9.200	6.800
Minimum	3.800	3.300	2.600	1.900
Standard Deviation	3.859	2.749	2.209	1.673
Geometric Standard Deviation	0.000	1.549	1.528	1.516

TABLE A-5. JUNE 1974 - LABORATORY COMPARISON

Nitrates

Geometric Mean Ratio	1.242	
95% Confidence Interval for Geometric Mean Ratio	(1.189, 1.297)	
Correlation Coefficient of Logs	0.9968	
Number of Observations	15	
	EMSL	RETA
Arithmetic Mean	558.800	519.120
Geometric Mean	479.062	385.780
Maximum	1762.000	1375.100
Minimum	94.000	79.200
Standard Deviation	114.869	89.003
Geometric Standard Deviation	1.218	1.215

TABLE A-6. JULY 1974 - LAB COMPARISON FOR SIDE-BY-SIDE CHESS SITES

Statistics	Sulfates	Nitrates
Geometric Mean Ratio	1.111	1.686
95% Confidence Interval for Geometric Mean Ratio	(0.993, 1.243)	(1.098, 2.588)
Correlation Coefficient of Logs	0.9462	0.2468
Number of Observations	23	23

	Rockwell	RETA	Rockwell	RETA
Arithmetic Mean	6.048	5.578	4.839	3.674
Geometric Mean	4.690	4.220	4.109	2.437
Maximum	21.600	16.300	13.000	17.100
Minimum	1.800	1.200	1.300	0.300
Standard Deviation	4.820	4.138	2.860	3.803
Geometric Standard Deviation	2.051	2.215	1.811	2.594

TABLE A-7. MAY 1973 - QUALITY CONTROL SPIKED SOLUTIONS FOR SULFATES MEAN RESPONSE AND 95% CONFIDENCE INTERVAL PER LABORATORY PER LEVEL

Concentration Level (µg/ml)	RETA	QAEML	# of Obs.
0	0.0 --	2.4 (2.1, 2.6)	5
30	24.8 (20.2, 29.4)	28.5 (27.6, 29.4)	5
60	47.0 (41.7, 52.3)	61.1 (52.1, 70.1)	5

TABLE A-8. DECEMBER 1973 - RETA ANALYSIS OF SPIKED SOLUTIONS

Sulfates

ANOVA Table

Factor	S.S.	d.f.	M.S.	F	p
Total	15977.9	31			
Day	101.3	3	33.7	2.42	0.087
Level	15487.9	1	15487.9	1111.34	0.000
Time	26.2	1	26.2	1.88	0.178
Error	362.3	26	13.9		

Level (µg/ml)	Mean Responses	# of Obs.
10	8.47 (7.41, 9.53)	16
60	52.47 (49.62, 55.32)	16

Nitrates

ANOVA Table

Factor	S.S.	d.f.	M.S.	F	p
Total	34.98	31			
Day	0.16	3	0.05	3.23	0.037
Level	34.27	1	34.27	2012.44	0.000
Time	0.10	1	0.10	5.94	0.020
Error	0.44	26	0.01		

Level (µg/ml)	Mean Responses	# of Obs.
1	0.195 (0.178, 0.212)	16
10	2.265 (2.151, 2.379)	16

TABLE A-9. NYCDAR-CHESS NO_3 DISCREPANCY STUDY
RETA AND QAEML ANALYSIS FOR NO_3 IN SOLUTIONS

Concentration Level (µg/ml)	QAEML	RETA (average of three)
4	3.75	4.20
6	5.90	5.90
9	9.00	8.50
11	11.00	10.60
14	14.10	13.47
16	16.10	14.20

TABLE A-10. JULY 1974 - ANALYSIS OF UNEXPOSED SPIKED FILTERS MEAN RESPONSES AND 95% CONFIDENCE INTERVALS AT EACH LEVEL

Concentration Level (µg/ml)	RETA	Rockwell	# of Obs.
	Sulfates		
3.00	1.84 (0.51, 3.17)	2.88 (2.55, 3.21)	5
11.26	9.24 (8.08, 10.40)	11.16 (10.53, 11.79)	5
15.18	12.64 (10.98, 14.30)	15.26 (13.71, 16.81)	5
27.76	22.16 (21.24, 23.08)	25.78 (25.35, 26.21)	5
36.00	24.90 (22.34, 27.46)	34.00 (32.96, 35.04)	5
	Nitrates		
3.05	2.40 (2.15, 2.65)	2.64 (2.53, 2.75)	5
6.04	4.80 (3.99, 5.61)	5.52 (5.38, 5.66)	5
9.01	7.95 (7.09, 8.81)	8.88 (8.74, 9.02)	5
12.00	8.94 (7.59, 10.29)	10.96 (10.82, 11.10)	5